# Mixture Design: Drying Times of Homemade Paint

**By Jessica Long**

The goal of my experiment was to determine what effects different proportions of ingredients in homemade paint would have on the drying time of the paint. The experiment used a four-component simplex centroid mixture design. I used flour, cornstarch, glue, and egg yolk as the ingredients. Each combination of ingredients was mixed with water and food coloring. The analysis of the results suggests that using only egg yolk resulted in the fastest drying time, while mixing flour and glue together gave the slowest. For pure blends, the fastest to slowest ingredients are egg, cornstarch, glue, and lastly flour. The final model I used for analysis had all linear terms and one quadratic term. Two of the results ended up being outliers, which may have influenced the final model. In a future experiment, I may want to replicate some of the points to reduce leverage, or add more interior points so I can get more information about possible nonlinear effects.

Paint for artists can be expensive and sometimes even toxic, so I wanted to try making my own non-toxic paints. Traditionally, there are many types of paints artists use, such as oil, acrylic, and watercolor, each with different properties. The paint the artist would choose would depend on what properties they want for a particular piece. For example, acrylic paint dries very quickly. This can be a positive or negative, as it allows for the artist to paint on top of layers quickly, but also makes it harder to blend. Acrylic also is thicker, which allows for creating interesting textures in paintings, but also makes it harder to clean up. Watercolor takes longer to dry, which allows for more techniques involving blending, but the colors are more transparent, making it harder to cover up mistakes. Oil takes even longer to dry, and is good for blending and building layers while having richer colors and thicker textures than watercolors. However, it is also more expensive, toxic, and harder to remove. With this in mind, I found several recipes online for making homemade paints using household materials. I was interested in whether using different ingredients would produce different properties, and which ingredients would result in what properties.

I decided to use flour, cornstarch, egg yolk, and glue as the varying ingredients, while also using water and blue food coloring for each paint-making attempt. I wanted to try different combinations of these ingredients to figure out which would result in the fastest and slowest drying time. I wanted to look at both ends of the spectrum as an artist would want to have both faster and slower drying paints for different purposes, as explored earlier. From previous experience, white glue takes a long time to dry, so I predicted it would take the longest to dry here as well. Egg tempera paint traditionally takes about 10-20 minutes. For the flour and cornstarch, I predicted they would thicken the paint, so it would dry faster. I also predicted the paints would be watery and transparent, like watercolor or tempera paints, due to the amount of water used and also the liquid nature of some of the ingredients.

I initially envisioned the experiment as a 2^4 factorial before realizing it was actually a mixture design, since I was mixing different ingredients together while maintaining a fixed ratio to water and food coloring. Specifically, the experiment is a four-component simplex centroid mixture design. Here, one unit is one tablespoon of the varying ingredient. As a remnant of the original factorial conception I originally listed all the runs, including the (0, 0, 0, 0) run in Yates order, and then randomized the run order (since the experiment would likely take place over several hours). I left the (0, 0, 0, 0) run in for reference.

For each ingredient included in the run, I added one tablespoon of the ingredient as well as two tablespoons of water and one drop of blue food coloring to the bowl. Once all the ingredients were added I would stir thoroughly with the paint brush. For example, if I were doing a blend with flour and egg yolk, I would add one tablespoon of floor, one tablespoon of egg yolk, four tablespoons of water, and two drops of food coloring. This way the 2:1 water:ingredient ratio is maintained. Two ingredients had extra preparation steps before being added. For the egg yolk, I had to separate the yolk from the whites (I used my hands and the eggshell). For the cornstarch, I heated it up in a pan on the stove with water, and removed one tablespoon of the resulting paste as soon as it started to solidify. After mixing, I used the paintbrush to evenly paint a 6cm x 6cm square on watercolor paper. This way each run would involve roughly the same amount of paint, so the total amount of ingredient present would also be the same. Unfortunately, sometimes the paint would still pool up in parts of the square. In these cases, I would gather the excess paint in one location of the square and not consider that portion when determining if the paint had dried. When the box was fully painted, I would start the timer. I judged the dryness of the paint based initially on appearance, then by touch. I stopped the timer when the paint would not come off when touched. Because it would take some time to assess whether the paint was dry or not, I rounded the time on the timer down to the nearest half-minute to use as my final response value. To prepare for the next run, I carefully washed the bowl, paintbrush, and spoon.

Here is the data collected from the experiment:

| | Label | Flour | Cornstarch | Glue | Egg | Run.order | Time.result | Minutes |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 5 | 13, 11 | 13.0 |
| 2 | 2 | 1.00 | 0.00 | 0.00 | 0.00 | 6 | 50, 15 | 50.0 |
| 3 | 3 | 0.00 | 1.00 | 0.00 | 0.00 | 9 | 36, 18 | 36.0 |
| 4 | 4 | 0.50 | 0.50 | 0.00 | 0.00 | 3 | 31, 20 | 31.0 |
| 5 | 5 | 0.00 | 0.00 | 1.00 | 0.00 | 12 | 44, 17 | 44.0 |
| 6 | 6 | 0.50 | 0.00 | 0.50 | 0.00 | 13 | 88, 50 | 88.5 |
| 7 | 7 | 0.00 | 0.50 | 0.50 | 0.00 | 4 | 20, 42 | 20.5 |
| 8 | 8 | 0.33 | 0.33 | 0.33 | 0.00 | 10 | 89, 20 | 89.0 |
| 9 | 9 | 0.00 | 0.00 | 0.00 | 1.00 | 2 | 9, 18 | 9.0 |
| 10 | 10 | 0.50 | 0.00 | 0.00 | 0.50 | 15 | 34, 29 | 34.0 |
| 11 | 11 | 0.00 | 0.50 | 0.00 | 0.50 | 8 | 19, 16 | 19.0 |
| 12 | 12 | 0.33 | 0.33 | 0.00 | 0.33 | 11 | 25, 20 | 22.0 |
| 13 | 13 | 0.00 | 0.00 | 0.50 | 0.50 | 7 | 33, 3 | 33.0 |
| 14 | 14 | 0.33 | 0.00 | 0.33 | 0.33 | 1 | 43, 24 | 43.0 |
| 15 | 15 | 0.00 | 0.33 | 0.33 | 0.33 | 14 | 25, 45 | 25.5 |
| 16 | 16 | 0.25 | 0.25 | 0.25 | 0.25 | 16 | 38, 24 | 38.0 |

At a glance, I noticed that all the dry times aside from the pure egg blend were larger than the reference run with just water and food coloring (13 min). The flour-glue and flour-cornstarch-glue runs were also much slower than all the others at 88.5 and 89.

To start with the analysis, I fitted the data to the linear, quadratic, and special cubic models for mixture designs. Here p=4, x1 = flour, x2 = cornstarch, x3 = glue and x4=egg.

**Linear**

$$E(y) = \sum_{i=1}^{p} \beta_i x_i \qquad \mathbf{(11.25)}$$

**Quadratic**

$$E(y) = \sum_{i=1}^{p} \beta_i x_i + \sum \sum_{i<j}^{p} \beta_{ij} x_i x_j \qquad \mathbf{(11.26)}$$

**Special cubic**

$$E(y) = \sum_{i=1}^{p} \beta_i x_i + \sum \sum_{i<j}^{p} \beta_{ij} x_i x_j + \sum\sum\sum_{i<j<k} \beta_{ijk} x_i x_j x_k \qquad \mathbf{(11.28)}$$

(From Montgomery - Design and Analysis of Experiments)

From Experiments with Mixtures (John Cornell) and Mixture Experiments in R Using mixexp (John Lawson, Cameron Willdon), standard regression methods such as lm in R do not provide the correct sums of squares when removing the intercept, as it is not corrected for the mean. This results in inaccurate F-test and R^2 results. The mixexp package provides a function MixModel that provides the correct coefficients, standard errors, and R^2. However, from some testing I found that it doesn’t work well with other functions in R such as anova(). It is possible to get an lm() fit with the correct sums of squares by removing one of the linear terms. In this model the intercept term corresponds to the coefficient for the removed term in the standard model, and the other coefficients reported are the coefficients for those terms minus the intercept term.

Linear model with MixModel():

```
   coefficients  Std.err   t.value        Prob
x1    64.911438 13.20098 4.9171676 0.0004589214
x2    26.680972 13.24288 2.0147416 0.0690366255
x3    58.180755 13.24288 4.3933626 0.0010749785
x4     5.281258 13.24288 0.3987999 0.6976731303

Residual standard error:  18.1282  on  11 degrees of freedom
Corrected Multiple R-squared:  0.5088609
```

Linear model with lm():

```
Call:
lm(formula = y ~ x2 + x3 + x4, data = df)

Residuals:
    Min      1Q  Median      3Q     Max 
-21.931 -12.399  -0.764   3.369  38.926 

Coefficients:
            Estimate Std. Error t value Pr(>|t|)    
(Intercept)   64.911     13.201   4.917 0.000459 ***
x2           -38.230     20.211  -1.892 0.085155 .  
x3            -6.731     20.211  -0.333 0.745378    
x4           -59.630     20.211  -2.950 0.013200 *  
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 18.13 on 11 degrees of freedom
Multiple R-squared:  0.5089,	Adjusted R-squared:  0.3749 
F-statistic: 3.799 on 3 and 11 DF,  p-value: 0.04314
```

Here the intercept is the x1 coefficient from the previous model, and the other coefficients are the appropriate differences. Note the R^2 values are close. The F-test is significant at level = 0.05. The t-tests show x1 and x3 are significant. Judging by the coefficients from MixModel(), the ingredients are ranked flour > glue > cornstarch > egg in terms of effect on drying time. In particular, the coefficient for egg is lower than the water only run (13).

Quadratic model with MixModel():

```
      coefficients  Std.err     t.value       Prob
x1       49.324181 16.42700  3.00262835 0.03000850
x2       33.882449 16.41182  2.06451451 0.09389239
x3       42.588699 16.41182  2.59500092 0.04854213
x4       11.104715 16.41182  0.67662890 0.52867243
x2:x1    -4.735740 71.09295 -0.06661335 0.94947109
x3:x1   196.198641 71.09295  2.75974815 0.03984657
x4:x1   -16.847649 71.09295 -0.23698059 0.82207513
x2:x3   -23.415178 70.97006 -0.32993036 0.75482691
x2:x4   -24.461468 70.97006 -0.34467306 0.74436471
x3:x4     2.472913 70.97006  0.03484445 0.97355205

Residual standard error:  16.59299  on  5 degrees of freedom
Corrected Multiple R-squared:  0.8129654
```

Additional results with lm():

```
Residual standard error: 16.59 on 5 degrees of freedom
Multiple R-squared:  0.813,	Adjusted R-squared:  0.4763 
F-statistic: 2.415 on 9 and 5 DF,  p-value: 0.1722
```

Here the p-value for the F-test > 0.05. The R^2 has increased notably to 0.813, but the adjusted R^2 has increased to a smaller value at 0.4763. The individual tests suggest only flour:glue is the only significant quadratic term. The coefficients suggest flour:glue and glue:egg have a positive/synergistic effect on drying time, while the other quadratic effects are negative/antagonistic. The linear coefficients maintain the same order as in the linear model.

Cubic model with MixModel():

```
          coefficients    Std.err    t.value      Prob
x1            50.02966   8.690311  5.7569476 0.1094904
x2            35.91873   8.689981  4.1333495 0.1511166
x3            43.91873   8.689981  5.0539498 0.1243585
x4             8.91873   8.689981  1.0263232 0.4917304
x2:x1        -44.61083  42.438788 -1.0511807 0.4841185
x3:x1        169.38917  42.438788  3.9913762 0.1562819
x4:x1         21.38917  42.438788  0.5040004 0.7027986
x2:x3        -74.38897  42.420485 -1.7536095 0.3299339
x2:x4        -10.38897  42.420485 -0.2449044 0.8470985
x3:x4         29.61103  42.420485  0.6980362 0.6120396
x2:x3:x1    1040.23153 286.462188  3.6313048 0.1710740
x2:x4:x1    -248.20101 286.462188 -0.8664355 0.5454798
x3:x4:x1    -507.00391 286.462188 -1.7698807 0.3274097
x2:x3:x4     -29.37124 286.555293 -0.1024976 0.9349751

Residual standard error:  8.690361  on  1 degrees of freedom
Corrected Multiple R-squared:  0.9897393
```

Additional results with lm():

```
Residual standard error: 8.69 on 1 degrees of freedom
Multiple R-squared:  0.9897,    Adjusted R-squared:  0.8563
F-statistic:  7.42 on 13 and 1 DF,  p-value: 0.2806
```

For this model, neither the F-tests nor the individual t-tests are significant. The flour:cornstarch:glue cubic term is positive, while the others are negative.

I decided to try a model with all the linear terms and the addition of the x1:x3 term to see if I can get a better fit. For this model I used lm() as MixModel only works for select model model types. Here the intercept term is the coefficient for x4/egg, and the other linear coefficients are the differences described previously.

```
Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept)    8.408      8.825   0.953  0.36318
x1            39.551     14.402   2.746  0.02061 *
x2            21.340     13.465   1.585  0.14410
x3            32.965     14.402   2.289  0.04510 *
x1:x3        198.683     51.334   3.870  0.00311 **
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 12.08 on 10 degrees of freedom
Multiple R-squared:  0.8018,    Adjusted R-squared:  0.7225
F-statistic: 10.11 on 4 and 10 DF,  p-value: 0.001531
```

The actual model is 47.959x1 + 29.748x2 + 41.373x3 + 8.408x4 + 198.683x1x3. We get a significant F-test result, and a higher adjusted R^2 than the linear or quadratic models. Only x1, x3, and x1:x3 are significant according to the t-tests, but I would like to look at the effects of all the ingredients.

F-test comparing to linear model:

```
Analysis of Variance Table

Model 1: y ~ x2 + x3 + x4
Model 2: y ~ x1 + x2 + x3 + x1:x3
  Res.Df    RSS Df Sum of Sq      F   Pr(>F)
1     11 3614.9
2     10 1458.7  1    2156.3 14.782 0.00324 **
```

The F-test is significant, so the new model improves on the purely linear model.

F-test comparing to quadratic model:

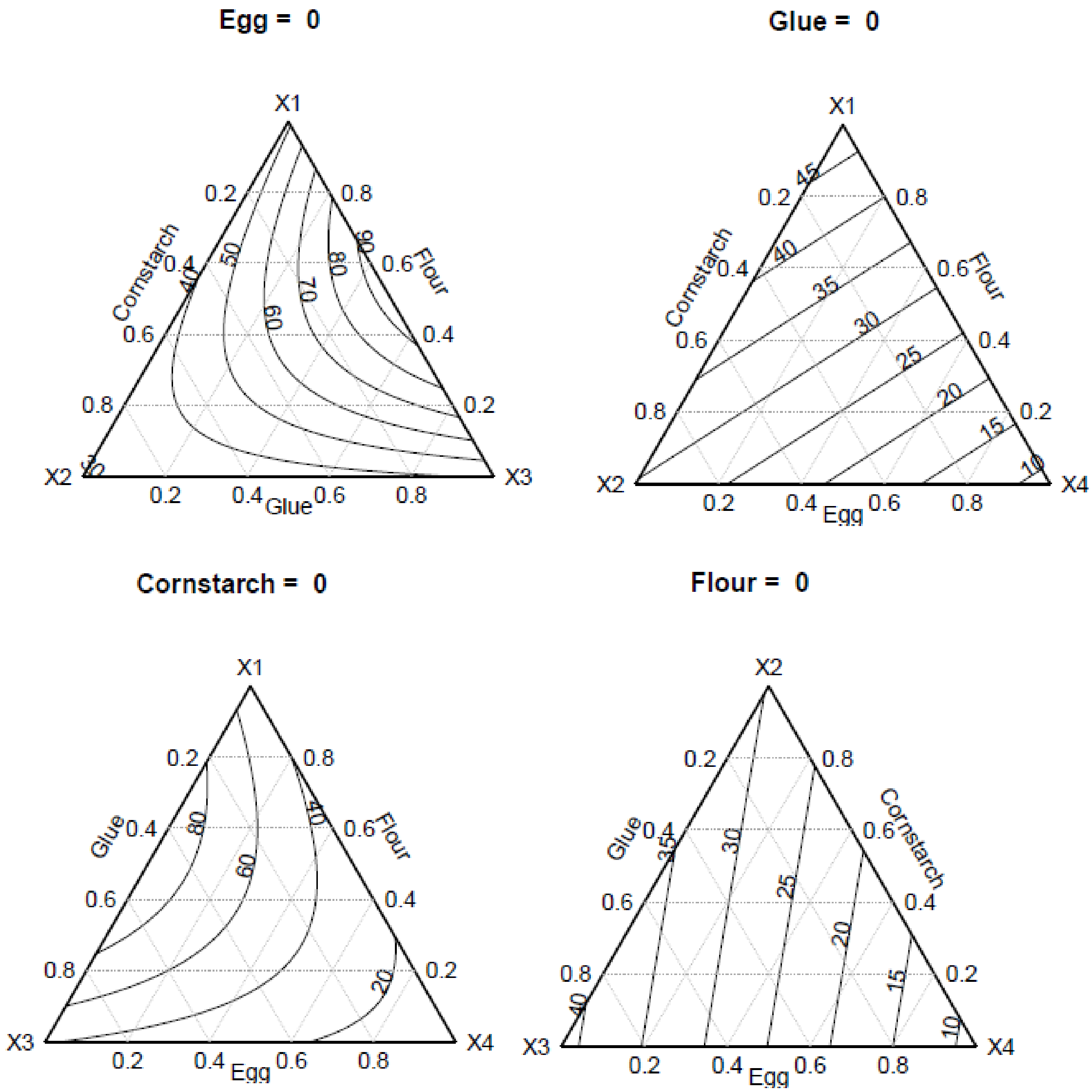
```
Analysis of Variance Table

Model 1: y ~ x1 + x2 + x3 + x1:x3
Model 2: y ~ x2 + x3 + x4 + x1:x2 + x1:x3 + x1:x4 + x2:x3 + x2:x4 + x3:x4
  Res.Df    RSS Df Sum of Sq      F Pr(>F)
1     10 1458.7
2      5 1376.6  5    82.049 0.0596 0.9962
```

The F-test is not significant, so the other quadratic terms can be left out.

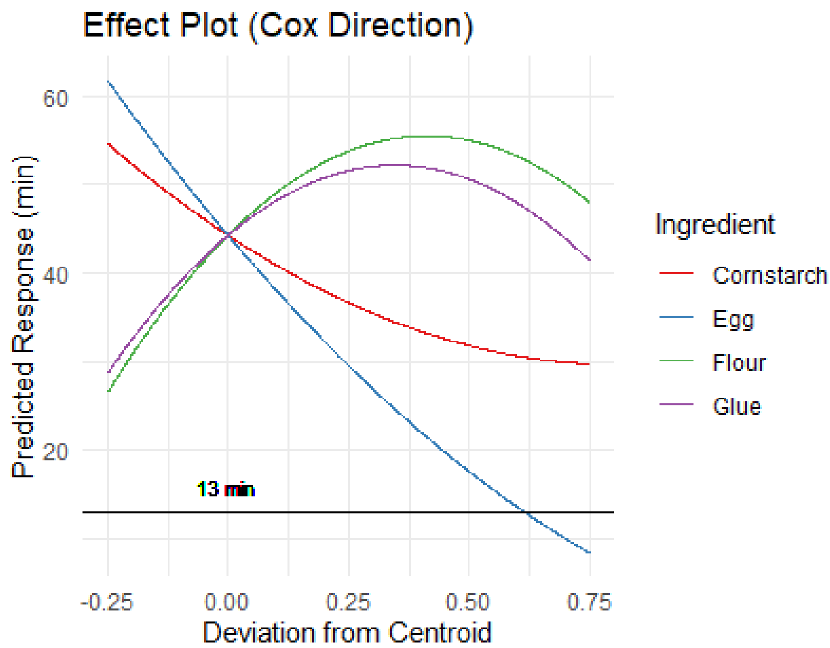
Here are the Cook's distance values for this model. The highest leverage points 2, 5, and 7 correspond to flour only, flour-glue, and flour-cornstarch-glue. From the data, the drying times for the flour-glue and flour-cornstarch-glue were much larger than the others, so this may have been an outlier.

```
           1            2            3            4            5            6            7 
3.394669e-02 1.347085e-01 3.645758e-02 5.619961e-02 4.024148e-01 1.340873e-01 2.759969e-01 
           8            9           10           11           12           13           14 
1.181031e-03 1.982166e-02 3.104411e-06 9.405017e-03 3.852591e-02 4.338432e-02 1.527428e-04 
          15 
5.115361e-03 
```

The mixexp package provides the ModelPlot function for plotting contour plots; however it can only show three components at once. I fixed the other component to be zero under the assumption that the quartic interaction would not be significant. The contours appear to be linear or quadratic depending on the components present, since there is only one quadratic term in the model. To minimize drying time, using only egg yolk would be the best choice. To maximize drying time, an even blend of flour and glue gives the longest time. Other values can be attained with various combinations.




I also made a response trace plot following Cornell's steps. The plot shows the predicted response along a line (the Cox direction) through the centroid and the vertex corresponding to one unit of a given ingredient and zero units of the others. Along this line, the values of the other ingredients maintain the same ratio to each other (1:1:1). This shows how the response changes with the proportion of one ingredient to the others. The response values are plotted against the deviation in the ingredient from the centroid. The vertex is at a deviation of 0.75. For egg and cornstarch, the drying time decreases as their proportion of the mixture increases. Egg yolk is the only ingredient to achieve response values below the water only result. For flour and glue, the maximum response occurs roughly between 0.3-0.4 deviation (i.e. 0.55-0.65 proportion), likely because these have synergy with each other that leads to longer drying times.




Aside from the time to dry, there were some other properties of the resulting paints that I noticed while conducting the experiment. The paints were similar to watercolors in transparency and fluidity as I had predicted. The pure egg paint has a shine to it that shows up to a lesser extent in the other egg blends. Because of the yellow, the paints including the egg yolk ended up having a greener hue. The glue paints have a smoother appearance than the others. The pure cornstarch paint turned out to be flaky once dried. This did not occur for the cornstarch mix blends. The paints using flour would include flour particles, leaving a textured effect. The particles also made it harder to paint and to clean the brush afterwards. I tried to blend more thoroughly to see if I could make the particles smaller or more even, but it did not work well. Overall, each ingredient added unique properties to the resulting paint. I particularly like the shine of the egg paint and the smoothness of the glue paint, and found these to be easier to paint with. I think the texture of the flour and cornstarch paints could be interesting to use if their flaws could be corrected, i.e. if the flour particles could be smaller and more even and if the cornstarch paint could maintain its texture without flaking.

There are some things I would try differently in a redo of the experiment. There is a possibility the flour-glue and flour-cornstarch-glue runs were outliers. From Cornell, we can make the leverage more uniform by having replicates. I could replicate each point, or even just a selection of points such as the vertices. Additionally, most of the nonlinear effects were not significant. I would like to see if I could get more information about the mixed blends. Aside from replication, I could also add more interior points to the design. Regarding the experimental procedure, I noticed that the watercolor paper I did the experiment on would bend after a while, which would make it harder to apply the paint evenly. There are ways to prevent this, which would be helpful in a redo. I also would try to see if I could mix the flour more thoroughly which could make the particles smaller, e.g. if I used something other than a paintbrush for mixing. This could change the properties of the flour paints.

# Appendix

### References


1. Douglas C. Montgomery - Design and Analysis of Experiments
2. D. R. Cox - A note on polynomial response functions for mixtures
3. John A. Cornell - Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data, Third Edition
4. John Lawson & Cameron Willden - Mixture Experiments in R Using mixexp


### Photos